NEGATIVE THERMAL IONIZATION MASS SPECTROMETRY OF OXYGEN IN PHOSPHATES.

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We report on an NTIMS technique for the isotopic analysis of $^{18}O/^{16}O$ and $^{17}O/^{16}O$ in phosphates, measured as PO_3^- ions. This contribution builds on earlier work (*1,2*) which showed that ion beams of PO_3^- and PO_2^- can be obtained from phosphate compounds. Since P is monoisotopic (^{31}P), the mass spectra of PO_3^- and PO_2^- reflect the oxygen isotopic composition and allow the routine measurement of all three oxygen isotopes. We show that it is possible to measure O isotope abundances in sedimentary, igneous and biogenic phosphates by a modified direct loading technique, without the need to convert phosphate oxygen to CO_2, as is necessary for conventional dual inlet Gas Isotope Ratio Mass Spectrometry (GIRMS).

Although oxygen isotope analysis by GIRMS is highly precise (±0.2λ, 2σ), relatively large volumes of sample gas (>0.1 µmole) are required to achieve source pressures high enough to maintain viscous flow through the capillary inlet and due to the low ionization efficiency of the electron impact source (0.01%). For NTIMS, we have obtained ionization efficiencies (IE) for PO_3^- >10% (PO_3^- ions detected/ PO_4 molecules loaded on the sample filament), readily permitting measurement of 70 ng of oxygen (100 ng PO_4). This corresponds to a cube ~30µm on the side. The precision and accuracy of the NTIMS oxygen isotope measurements depend on: 1) eliminating isobaric interferences from $^{79}Br^-$ and $^{81}Br^-$; 2) evaluating the potential for high temperature O-exchange between PO_4 oxygen, and extraneous oxygen on the filament or within the mass spectro-meter source chamber; and 3) controlling the effects of instrumental isotope fractionation.

We have performed extensive tests of sample preparation and loading techniques and have adopted the following procedure. A thin layer of colloidal Pt powder (Pt-black) is loaded as an aqueous slurry on a Pt filament (0.5mm wide x 0.03mm thick x 1.2cm long) using an adjustable microsyringe fitted with polyethylene microtubing (PE-10); the slurry is dried. An aliquot of an ammoniacal Ag_3PO_4 solution (10% NH_4 OH) is loaded onto the Pt filament, within the Pt-black covered area, and heated gently. The PO_4 con-centration of the solution is chosen so that 0.25µl is dispensed. As the solution evaporates, Ag_3PO_4 crystals precipitate within the area covered by the Pt powder. It is important to achieve a uniform load, and not to allow the sample to spread outside the area covered by the Pt powder (3mm). To reduce the work function of the filament, Ba is loaded on top of the Ag_3PO_4 as spectroscopically pure $BaCl_2$ (in water). Again, it is important to achieve a uniform $BaCl_2$ layer which covers the Ag_3PO_4, but does not extend beyond the area covered by the Ag_3PO_4 crystals. Enough $BaCl_2$ is added to correspond to a 1:1 molar ratio of Ba:PO_4. This mixture produces intense PO_3^- ion beams and no accompanying Cl^- or Br^- ion beams. This eliminates the mass interferences at 79 and 81 amu from Br^-. Use of excess $BaCl_2$ relative to PO_4 (e.g., 1.5:1) results in significant Cl^- ion beams, which can be accompanied by Br^- ion beams. Elimination of Br interferences works for samples down to 100 ng of PO_4. For smaller samples, controlling the intimate mixing of $BaCl_2$ and Ag_3PO_4 on the filament is problematic;we have not yet eliminated Br interference at the level of 10 ng PO_4.

Using the above loading procedure, a $P^{16}O_3^-$ ion beam is first observed at temperatures <776°C (detection limit of optical pyrometer). Data acquisition starts when the $P^{16}O_3^-$ ion current is $5x10^{-11}$ A. The PO_3^- ion beam is either stable or increases in intensity throughout the run and, typically, we observe no halogen ion beams during data collection. At the beginning of data acquisition, we observe typical PO_3^-/ PO_2^- ratios of ~500, decreasing to ~250 by the end of a 4-5 hour analysis. No other species are observable. Therefore, there is no direct evidence that species other than PO_3^- contribute to oxygen loss from the filament. Filament temperatures are nearly constant during each run, but vary from sample to sample (<776 to 860 °C for the 1µg loads). Smaller samples (1-10 ng) run at a higher temperature of ~960 °C. The PO_4 loading blank was determined using several emitters [$Ba(OH)_2$, $Ba(NO_3)_2$, $BaCl_2$] each loaded using Pt-black. Although intense halogen beams formed in all cases, we observed no PO_3^- or PO_2^- beams, indicating that the filament loading blank for phosphate is negligible. We have also checked, by using $BaSO_4$, that there is no interference at mass 80 ($P^{17}O^{16}O_2^-$) from $^{32}S^{16}O_3^-$.

Using H_2O highly enriched in $^{17,18}O$, we have investigated the possibility of oxygen isotope exchange between PO_4 and oxygen present in the sample solutions, or adsorbed on the filament, or from the mass spectrometer source, at the temperature range of thermal ionization of PO_3^-. We have found that O-exchange is less than 1% and negligible at the present level of external precision. If it is assumed that the main source of extraneous O is laboratory water with a $\delta^{18}O$ = -10 λ, the shift to PO_4 oxygen is <-0.1λ.

The ionization efficiency of PO_3^- is >10% compared to 0.01% for both GIRMS and secondary ion

mass spectrometry (SIMS). Therefore, NTIMS analysis of O isotopes offers exceptional sensitivity enabling routine and precise O isotope analysis of sub-microgram samples of PO_4 (<21 nmoles equivalent CO_2 gas) without need for lengthy chemical pretreatment of the sample. The NTIMS technique allows the routine measurement of both $^{18}O/^{16}O$ and $^{17}O/^{16}O$ in phosphate. Overall external precision is $\pm 1\lambda$ (2σ) for $^{18}O/^{16}O$ and $^{17}O/^{16}O$ with reproducibility of instrumental isotope fractionation of $\pm 0.5\lambda$ amu^{-1}. We have not achieved the external precision of 0.2λ reported for GIRMS. We show the data obtained by NTIMS in Fig. 1. Data include analyses of Johnson and Matthey reagents (Ag_3PO_4 and Na_3PO_4, converted to Ag_3PO_4 by us) and of apatite standards: igneous apatites UMS-1 (University of Michigan standard, provided by J. R. O'Neil) and LA-1 [Laramie Anorthosite, provided by J. Farquhar (*8*)] and Florida rock phosphate (SRM-120c, available from NIST). The data follow a well defined isotope fractionation line. This is displaced by 23λ from the oxygen analyses by Nier(*3*), used to define SMOW. We note that ion probe data (*4*,*5*) are consistent with the oxygen isotope fractionation line defined by NTIMS. If we use the value for $^{18}O/^{16}O$ measured by Baertschi (*6*) for Vienna-SMOW (V-SMOW) to establish a consistent oxygen isotope composition by NTIMS we obtain, for $^{18}O/^{16}O = 0.0020052 \pm 0.000005$, the corresponding value $^{17}O/^{16}O = 0.0003820 \pm 0.0000004$. We define this oxygen isotope composition as POT (for PO-Three). We consider this composition to be precise and self-consistent, within an isotope fractionation factor. It should represent the most reliable isotope abundances for O. If we use the POT composition to calculate $\delta^{18}O_{POT}$ values for NTIMS data and the V-SMOW composition to calculate $\delta^{18}O_{V\text{-}SMOW}$ values for data obtained by GIRMS, we can compare the data for consistency. The results are shown in Fig. 2 for the LA-1, UMS-1 and SRM120c standards. Careful evaluation of the $\delta^{18}O_{V\text{-}SMOW}$ values indicates the need for a further adjustment, because the value for LA-1 has been obtained using the standard BrF_5 technique, while the data on UMS-1 and SRM120c have been obtained by a modified technique (*7*). In Fig. 2 we have shown the $\delta^{18}O_{V\text{-}SMOW}$ data on UMS-1 and SRM120c as reported in (*7*) and corrected by 2λ, although this correction is somewhat uncertain. This is discussed in some detail in (*7*). With these considerations, we find good agreement between NTIMS and GIRMS $\delta^{18}O$ data, consistent with a uniform offset between the $\delta^{18}O_{POT}$ and $\delta^{18}O_{V\text{-}SMOW}$ results. More tests of phosphate standards will be reported.

The NTIMS technique is ideally suited to analysis of small phosphate samples including single mineral grains of meteoritic and terrestrial phosphates or of apatite microfossils.

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Fig. 1. (top) NTIMS data for 3 standards and 2 normals. (bottom) Comparison with other measurements of the absolute composition of oxygen. Note agreement with SIMS data and shift of the NTIMS and SIMS data relative to the Nier (1950) data, equivalent to $\delta^{17}O=23\lambda$.

Fig. 2. Comparison of NTIMS $\delta^{18}O_{POT}$ and GIRMS $\delta^{18}O_{V\text{-}SMOW}$. The data are consistent with a slope one line. A possible correction for GIRMS data obtained by phosphate thermal decomposition is shown (see text).